

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 8.00

Microfiche (MF) 1.65

653 July 65

THE ROLE OF RADIATION IN PRIMORDIAL ORGANIC SYNTHESIS

Cyril Ponnamperna

Exobiology Division

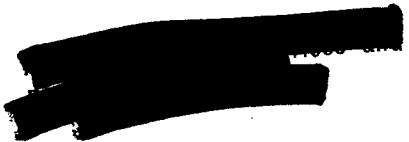
National Aeronautics and Space Administration

Ames Research Center

Moffett Field, California

FACILITY FORM 602

N 68-27635	(THRU)
(ACCESSION NUMBER)	
26	(CODE)
(PAGES)	
TMX-57965	04
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)



THE ROLE OF RADIATION IN PRIMORDIAL ORGANIC SYNTHESIS

Several hypotheses have linked the origin of life on earth with the gradual formation of compounds biological significance. A long chemical evolution has been considered to be a necessary preamble to the origin of life. Oparin in his early writings alluded to the simple solutions of organic substances whose behavior was governed by the properties of the component atoms and their arrangement in the molecular structure. (1) According to him, increasing complexity resulted in new properties and biological orderliness thus came into prominence. Haldane had speculated on the production of a vast variety of organic substances including sugars and some of the materials from which proteins are built up, by the action of ultraviolet light on the earth's primitive atmosphere. (2) Two things, therefore, appear to be necessary for the sequence of events which led to the appearance of the first replicating molecules:

1. The origin of the monomers
2. The condensation of these monomers into polymers capable of replication.

The starting point for any discussion on the question of the origin of life must turn around the nature of the earth's primitive atmosphere. For it is this atmosphere which supplied the raw materials. The present rarity of the terrestrial noble gases with respect to their cosmic distribution indicates that a primary atmosphere of the earth was almost completely lost in

2.

early times and that the present atmosphere is of secondary origin. The elements which were later to form a secondary terrestrial atmosphere must have rained out of the primary atmosphere in compounds or have been accumulated as gases during the formation of the earth. As the temperature of the newly-formed planet increased through the energy of accretion and due to radioactive decay these compounds were decomposed and the occluded gases released. The chemical composition of the secondary atmosphere must, at first, have been similar to that of the primary atmosphere. Because of its high rate of escape, most of the free hydrogen must have been lost and the principle constituents of the atmosphere must have been water vapor, ammonia, and methane. It is this atmosphere of water vapor, methane, and ammonia, and small amounts of hydrogen which will be considered in this discussion as the primitive atmosphere of the earth.

Although there is some controversy about the true nature of the earth's early atmosphere, the evidence available from several sources suggests that the primitive atmosphere must have been reducing in nature. (3,4) The great abundance of hydrogen in the universe is the basic argument in support of this theory. Over 90% of the known universe is made up of free hydrogen. The equilibrium constants further indicate that in the presence of an excess hydrogen the elements carbon, nitrogen, and oxygen must have been present in their reduced form as methane, ammonia, and

water. (Table 1) From planetary spectroscopy we learn that the major planets Jupiter and Saturn which have retained their primitive atmosphere have a large abundance of methane, ammonia, hydrogen, and water. The meteorites which have the approximate age of the earth contain metals in the reduced form. An added argument which indirectly supports the idea that the primordial atmosphere must have been reducing is that many of the molecules which are necessary for living organisms cannot be produced unless we have non-oxidizing conditions.

The energies available for the synthesis of organic compounds under primitive earth conditions were ultraviolet light from the sun, electric discharges, ionizing radiation, and heat. (4) While it is evident that sunlight is the principle source of energy, only a small fraction of this was in the wavelength below 2,000 Å, which could have been absorbed by the methane, ammonia, and water. However, the photodissociation products of these molecules could absorb energy of higher wavelengths. Next in importance as a source of energy are electric discharges such as lightning and corona discharges from pointed objects. These occur close to the earth's surface and hence would more efficiently transfer the reaction products to primitive oceans. A certain amount of energy was also available from the disintegration of U^{235} , U^{238} and K^{40} . While some of this energy may have been expended in the solid material such as rocks, a certain proportion of it was available in the oceans and the atmosphere.

Heat from volcanoes was another form of energy that may have been effective in primordial synthesis.

A glance at the complete electromagnetic spectrum shows us the distribution of radiation from gamma rays on the one hand through X-rays, ultraviolet rays, visible, infrared to radio and power waves. It is the energy in the shorter wavelength region of this spectrum that we are most interested in. We shall, therefore, limit ourselves to two aspects of radiation, short wavelength ultraviolet light and ionizing radiation.

(Figure 1)

The light which was most effective in the synthesis of organic compounds must have been in the region in which the methane, ammonia, and water could be excited. The range in which these molecules absorb is illustrated in Figure 2.

The best region for absorption and for dissociation of these molecules would be between 1,000 and 2,000 Å. Urey's calculations show that the energy available from the sun below 2500 Å is around 570 calories per square centimeter per year. (Table 2) Below 2,000 Å it is only 85 and below 1500 Å it is only 16. (4) However, if the dissociation of these molecules took place the products formed could absorb light at longer wavelengths. We know that when methane is dissociated, the methyl radical begins to absorb around 2500 Å. The methyl radical can be further dissociated into methylene and hydrogen and methylene absorbs

around 2800 Å. Once molecules like the purines and pyrimidines are synthesized, they will absorb light around 2600 Å and become effective in further organic synthesis. (5)

The largest amount of energy, however, is in the longer wavelengths. In the region greater than 2500 Å the total energy amounts to 260,000 cals per square centimeter per year on the earth's surface. In order to absorb these energies we need molecules like the porphyrins. Here we have the beginnings of photosynthesis.

The evolution of photosynthesis raises the question of oxygen in the atmosphere. Free oxygen is unique in our planetary system. The oxygen in the present atmosphere appears to have arisen from two sources, the photodissociation of water in the upper atmosphere by short wave length ultraviolet light, and by plant photosynthesis. Photosynthesis probably evolved when the ozone layer in the upper atmosphere cut out the ultraviolet light from the sun and thus put an end to the photochemical synthesis of organic compounds in the primitive environment. Heterotrophs which thrived on photochemicals available around them were converted to the autotrophs which had to photosynthesize their own food. This change may be diagrammatically represented by the hour glass. (Figure 3) Only those organisms that could incorporate molecules such as porphyrins and make use of longer wavelength light were able to pass through the bottleneck. There was a wholesale massacre at this junction. The organisms that survived and developed further were able to evolve into the wide

variety of life on earth today.

When we turn our attention to ionizing radiation, we find that the principle radioactive sources on the earth are potassium 40, uranium 238, uranium 235, and thorium 232. Potassium 40, seems to be quantitatively more important than the other three sources at present and, therefore, must have been even more important in the past. The energy of potassium 40 is in the form of penetrating beta and gamma rays. Almost 90% of the energy from uranium 238 and thorium 232 is carried by α particles which may not be penetrating enough to have a significant effect. Calculations show that the decay of potassium 40 in the earth's crust today is 3×10^{19} calories per year. 2.6 million years ago this would have been 12×10^{19} calories per year. By comparison, this is only 1/30 the amount of energy available from shortwave ultraviolet light below 2500 Å. (6)

The distribution of the energy is a matter of importance. Most of the radiation from the radioactive sources is absorbed in solid matter. Since the earth's crust is about 30km thick, this type of radiation could not have made a contribution to organic synthesis in the primitive atmosphere. However, local regions of high activity might have existed in the past. There may have been microenvironments where the catalytic action of the minerals favored condensation reactions of the first formed molecules. The role of clay in organic synthesis has been widely recognized.

(7)

There are numerous investigations on the radiation chemistry and the photochemistry of gases (Tables 3 and 4), some of which have a direct bearing on the problem of the origin of life. One of the first experiments was that of Garrison and his co-workers. (8) Carbon dioxide and water were irradiated with particles in the Berkeley cyclotron. Formaldehyde, formic acid, and succinic acid were formed. In 1957, Dose and Rajewsky irradiated a mixture of ammonia, water, methane, hydrogen, carbon dioxide and nitrogen with X-rays and gamma rays, and demonstrated by electrophoretic separation is that some amino acids were also produced. In the same year, Hasselstrom irradiated a solution of ammonium acetate with β particles and identified glycine, aspartic acid, and diamino-succinic acid. (10) In 1961, Berger irradiated the simulated primitive atmosphere with protons and obtained urea, acetamide, and acetone. (11) Palm and Calvin, irradiated methane, ammonia, and water with 5 mev β particles from a linear accelerator. In this experiment they identified urea, lactic acid, alanine, and glycine. Hydrogen cyanide was found to be an important intermediate. (12) Oro, in the same laboratory, used the identical equipment for the irradiation of methane, ammonia, and water. In some experiments, the ammonia was replaced by nitrogen and the methane by ethane. His analysis indicated that several amino acids and hydroxy acids were formed. (13)

Among one of the first photochemical experiments was that of Bahadur. (14) He irradiated formaldehyde and certain inorganic

salts such as potassium nitrate and ferric chloride with visible light. Aspartic acid, serine, and lysine were identified. This experiment may not be too relevant to early conditions on account of the use of nitrate which may not have been consistent with the reducing conditions of the primitive earth. In 1957 Groth and Weysenhoff reported their experiments with methane, ammonia, and water or ethane, ammonia, and water, using the 4070 Å and 2196 Å lines. Glycine, alanine, aminobutyric acid, formic acid, and acetic acid were synthesized. (15) At the first International Symposium on the Origin of Life held in Moscow in 1951, Terenin reported that when he irradiated methane, ammonia, and water, in the Schuman region, he found alanine and other acids. (16) Reid, at the same meeting, described the use of the 1849 Å wavelength for the irradiation of formaldehyde, ammonia, and carbon dioxide, in the presence of some inorganic salts. Glycine, alanine, and formic acid were identified. (17) Pavloskaya and Pasynskii claimed that when formaldehyde in the presence of ammonium nitrate or ammonium chloride was irradiated with a high pressure mercury lamp, they could obtain serine, glycine, glutamic acid, alanine, and valine. (18) More recently, Dodonova and Sidorova used methane, ammonia, water, and carbon monoxide, in the region between 1450 to 1800 Å. Several amino acids, including glycine, alanine, valine, leucine, and some amines such as methylamine, ethylamine, were identified. Hydrazine, urea, and formaldehyde also appear to be formed. (19)

In our own laboratory several experiments have been conducted with both ionizing radiation and ultraviolet radiation. (20) In the experiments starting with methane, ammonia, and water, an electron beam was used to simulate potassium 40 on the primitive earth. Mixtures of methane, ammonia, and water were irradiated with 4.5 mev electrons from a linear accelerator in the Lawrence Radiation Laboratory of the University of California at Berkeley. In a 45 minute period, the total energy absorbed was 7×10^{10} ergs per gram. The results of this investigation clearly established that adenine was a product of the radiation of methane, ammonia, and water. It also appears that the production of adenine is enhanced by the absence of hydrogen. This is not surprising since methyl carbon must be oxidized in order to appear finally in purines. In any event, a high concentration of organic matter on the prebiotic earth probably arose when most of the hydrogen had escaped.

In later experiments, we used two other radiation sources, an γ cell 220 manufactured by Atomic Energy of Canada with an intensity of 3.3×10^5 rads per hour and another Cobalt 60 source located at the Nuclear Medicine Center of the University of California at Los Angeles. This had an intensity of 4×10^6 rads per hour. In the first series of experiments, we had no way of protecting the end products from the radiation. What we were measuring was an equilibrium condition between the organic chemicals synthesized

and our starting materials. In the second series, however, the arrangement of the cobalt 60 pencils permitted the synthesis to take place in one region and the end products were carried away and accumulated in another. With the aid of radioactive carbon, we were able to show by paper chromatographic analysis that a wide variety of organic compounds were formed. Among these, hydrogen cyanide and formaldehyde were identified.

Our next attempts were to use ultraviolet light for the irradiation of the mixture of methane, ammonia, and water. A dumb-bell shaped glass apparatus was employed. The upper flask contained the primitive atmosphere of methane, ammonia and water and the lower flask represented the ocean. A window on the upper flask let in the ultraviolet light. A spectrum from 1,000 Å to 2,000 Å was obtained from a helium lamp at one atmosphere pressure discharged at 10,000 volts. While this lamp gave us the energy in the right region, the total amount of energy absorbed was 10^{10} photons per square centimeter. At the end of a 48 hour experiment the total yield was only a quarter of a percent. However, recently much more powerful sources have been available. By the use of vortex stabilized plasma, a source has been developed which gives 10^{19} photons per square centimeter per second for the interval between 1,050 Å to 2,000 Å. Argon gas at 14 atmospheres is used with an input power of 17 watts. The irradiance calculated here is based on the transmission through a six millimeter-thick lithium fluoride window.

It is to be expected that the use of lithium fluoride poses a problem in experiments where one of the materials irradiated is water. However, we have overcome the difficulty to some extent by keeping the window above 100° . After a period of 48 hours the window has to be changed.

Since hydrogen cyanide is an important intermediate when a mixture of methane and water was exposed to electric discharges or ionizing radiation, in a third series of experiments we used it as the starting material. Miller and Urey considered that hydrogen cyanide was an intermediate in their synthesis of amino acids from primitive mixtures. Palm and Calvin identified hydrogen cyanide as a major product when a mixture of methane, ammonia and water was irradiated with electrons. The use of hydrogen cyanide as starting material is also strengthened by the theory that comets may have been responsible for the accumulation of relatively large amounts of carbon compounds on the primitive earth. Some of these compounds are known to be transformed spontaneously into amino acids and other biochemical materials. The CN band is generally the first molecular emission to appear on the tails of comets during the travel of these bodies towards the sun. It is also the band with the largest degree of extension into the comet's heads. It is possible that the heads of comets contain frozen free radicals which are volatilized by radiant heat from the sun. It is also possible that they contain frozen molecules which are vaporized and photodissociated into radicals by solar radiation. (21)

When hydrogen cyanide in dilute solution containing 10^{-3} moles per liter was exposed to ultraviolet light and the products examined, a large number of discrete organic molecules were formed. Further analysis showed that adenine, guanine, and urea had been synthesized in this experiment. Approximately 6% of the starting material appears as non-volatile products. About one percent of this is adenine, 0.5 per cent guanine, and about 10 per cent is urea.

Several mechanisms have been suggested for the synthesis of purines from hydrogen cyanide. According to Kliss and Matthews (22) the HCN dimer aminocyanocarbene can exist in its 1,1 and 1,3 forms. In its 1,3 form it could give rise to cyclic bases such as purines. Oro has suggested a series of base catalyzed reactions for the synthesis of adenine. Formamidine and 4-amino-imidazole 5-carboximidine are the key intermediates which, in the final step, give rise to adenine. (23) Recent work by Orgel and co-workers have shown that aminomalonitrile is an important intermediate in the synthesis of adenine. The monoaminomalonitrile is transformed into 4-aminoimidazole 5-carboximide, either by direct reaction with formamidine, or what is most interesting for our studies, the photochemical rearrangement of the hydrogencyanide tetramer. By hydrolysis it can give the 4-amino-imidazole-5-carboxamide which can condense under mild conditions with aqueous cyanide, formamidine, or cyanogen to give us a variety of purines: adenine, hypoxanthine, diaminopurine, and guanine. (24) (Figure 4)

Since formaldehyde is one of the products of the irradiation of methane, ammonia, and water, we performed a third series of experiments using formaldehyde as our starting material. In basic solution, formaldehyde polymerizes to give the higher sugars. When formaldehyde in very dilute solution was exposed to ultraviolet light and ionizing radiation, several sugars were formed. By careful chromatography, we have been able to identify the sugars, ribose and deoxyribose. A preliminary separation into groups of sugars seems to indicate that by far the highest yield is of the pentoses and hexoses. This is no doubt due to the inherent stability of the five and six membered rings. It is interesting to note that the action of ultraviolet light or gamma rays is somewhat similar in effect to the polymerization of formaldehyde by basic media, a reaction that has been known to organic chemists for over a hundred years.

In the series of experiments so far described, we have been able to establish the formations of the purines, adenine and guanine, and the sugars, ribose and deoxyribose. It was, therefore, of interest to see whether the same radiation which was responsible for the synthesis of these compounds could also be instrumental in the condensation reactions needed to produce nucleosides and nucleoside phosphates. It has been suggested that the earth's primitive reducing atmosphere was at least slightly transparent between 2,400 Å and 2,900 Å and that the activation of ultraviolet absorbing purines and pyrimidines was a possible step in the

formation of nucleosides and nucleotides. The argument for this transparency is as follows: Formaldehyde absorption extends longwards of 2,900 Å; acetaldehyde and acetone throughout the 2,400 Å to 2,900 Å region; ammonia, acetylene, and other molecules absorbed below 2,400 Å. The question of the transparency of the primitive terrestrial atmosphere depends on the abundance of acetaldehyde and acetone. Because of the relatively low yield of acetaldehyde and acetone in simulation experiments, it seems likely that the early reducing atmosphere was at least slightly transparent between 2,400 Å and 2,900 Å. From models of the evolution of the sun, the ultraviolet flux in the wavelength between 2,900 Å and 2,400 Å incident on the earth's atmosphere 4 billion years ago, is computed to be 7×10^{14} photons per square centimeter per second. Even with substantial atmospheric absorption, ultraviolet radiation in this window would have greatly exceeded other energy sources for organic synthesis and would have been strongly absorbed by purines and pyrimidines if they were present in the early oceans.

Our simulation experiments were in four different categories. In the first, the starting material was adenine; in the second, adenosine; in the third, adenosine monophosphate; in the fourth, adenosine diphosphate. The conversion of adenine to adenosine, adenosine to adenosine monophosphate, monophosphate to diphosphate, and the diphosphate to triphosphate has been established. Experiments using adenine as starting material have produced

adenosine, the monophosphate, the diphosphate, and the triphosphate. Adenosine is not produced in detectable amounts in the absence of a phosphorous compound. While adenosine is produced in the presence of both phosphoric acid and ethylmetaphosphate, the nucleoside phosphates were detected only with the use of the metaphosphate. The metaphosphate may not be a likely source of phosphorous on the primitive earth, but the result clearly established that the process could occur abiogenically. (25)

The yields achieved in our experiments appear to be reasonable in the context of chemical evolution. The quantum yield for a one-hour irradiation is approximately 10^{-5} for the formation of adenosine from adenine and ribose, and almost an order of a magnitude greater for the nucleotides. A luminescence assay using dehydrated fire-fly tails and a hexokinase assay established that the ATP synthesized by us was identical with commercially available ATP.

We have also investigated the photochemical synthesis of peptides. When an aqueous solution of glycine and leucine was exposed to ultraviolet light in the presence of cyanamide, the dipeptides glycyl-glycine, glycl-leucine, leucly-glycine, leucyl-leucine, and some tripeptides were formed. The action of cyanamide may be analogous to that of dicyclohexylcarbodiimide which has been extensively used by Khorana and his co-workers for the synthesis of nucleotides. (26)

These results show that under simulated primitive earth conditions, molecules of biological significance can be synthesized by the action ionizing or ultraviolet radiation. They lend support to the hypothesis of chemical evolution, since not only can primary molecules be made by this process but, once made, they can undergo condensation reactions to form complex compounds. As the laws of chemistry and physics are universal laws these laboratory experiments point out that, wherever the right conditions exist, those molecules which can act as precursors of biological systems will arise anywhere in the universe.

References

1. A. I. Oparin, in Origin of Life. (Macmillan, New York, 1938)
2. J. B. S. Haldane, Rationalist Annual 148 (1938).
3. H. C. Urey, in The Planets. (Yale University Press, Newhaven, Connecticut, 1952).
4. S. L. Miller and H. C. Urey, Science 130, 245 (1959).
5. H. C. Urey, Proc. Natl. Acad. Sci., U.S. 38, 351 (1952).
6. A. J. Swallow, in Radiation Chemistry of Organic Compounds. (Pergamon, Oxford, 1960), p. 38, 351.
7. L. Heller and A. Weiss, Eds., in Proceedings of the International Clay Conference. (Israel Program for Scientific Foundation, Jerusalem, Israel, 1966).
8. W. M. Garrison, J. G. Hamilton, D. C. Morrison, A. A. Benson and M. Calvin, Science 114, 416 (1951).
9. K. Dose and B. Rajewsky, Biochem. Biophys. Acta. 25, 225 (1957).
10. T. Hasselstrom, M. C. Henry, and B. Murr, Science 125, 350 (1957).
11. R. Berger, Proc. Natl. Acad. Sci., U.S. 47, 1434 (1961).
12. C. Palm and M. Calvin, J. Am. Chem. Soc. 84, 2115 (1962).
13. J. Oro, Nature 197, 971 (1963).
14. K. Bahadur, Nature 173, 1141 (1954).
15. W. Groth and H. Van Weyssenhoff, Naturwiss 44, 510 (1957).

16. A. N. Terenin, in Proceedings of the First International Symposium on the Origin of Life on Earth, Moscow. (Pergamon Press, London, 1959), p. 136.
17. C. Reid, Ibid, p.619.
18. T. E. Pavloskaya and A. G. Passynsky, Ibid, p. 151.
19. N. Y. Dodonova and A. L. Sidowa, Biophysics (a translation of Biofizika) 6, 14 (1961).
20. C. Ponnampерuma, in The Origins of Prebiological Systems and of Their Molecular Matrices, S. W. Fox, Ed. (Academic Press, New York, 1965), p. 221.
21. J. Oro, Nature 190, 389 (1961).
22. R. H. Kliss and C. N. Matthews, Proc. Natl. Acad. Sci., U.S. 48, 1300 (1962).
23. J. Oro and A. P. Kimball, Arch. Biochem. Biophys. 93, 166 (1961).
24. R. Sanchez, J. Ferris and L. E. Orgel, Science 153, 72 (1966).
25. C. Ponnampерuma, C. Sagan, and R. Mariner, Nature 199, 222 (1963).
26. H. G. Khorana, in Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest. (John Wiley, New York, 1961).

ELECTROMAGNETIC SPECTRUM

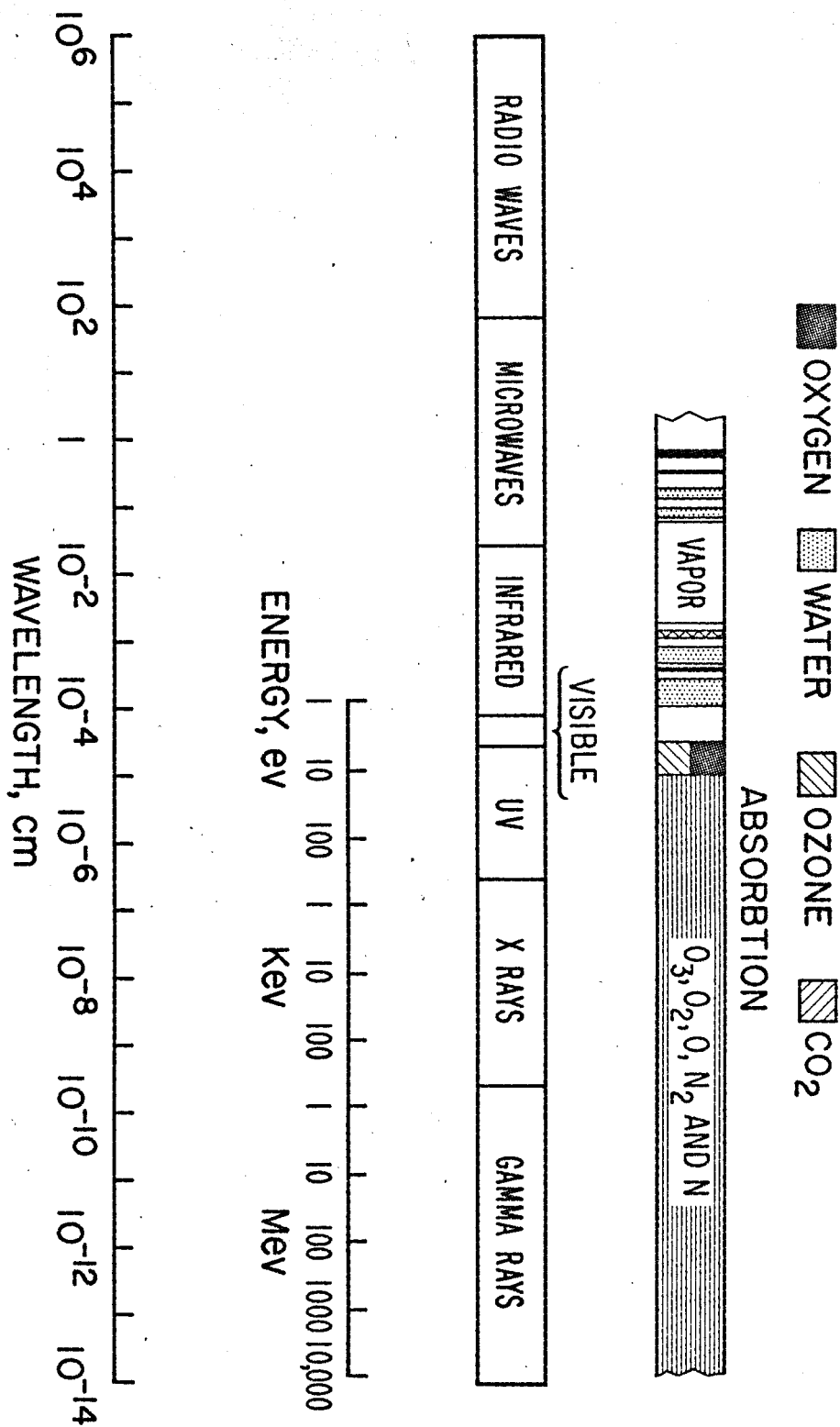


Figure 1

ABSORPTION RANGES OF CH₄, NH₃ AND H₂O

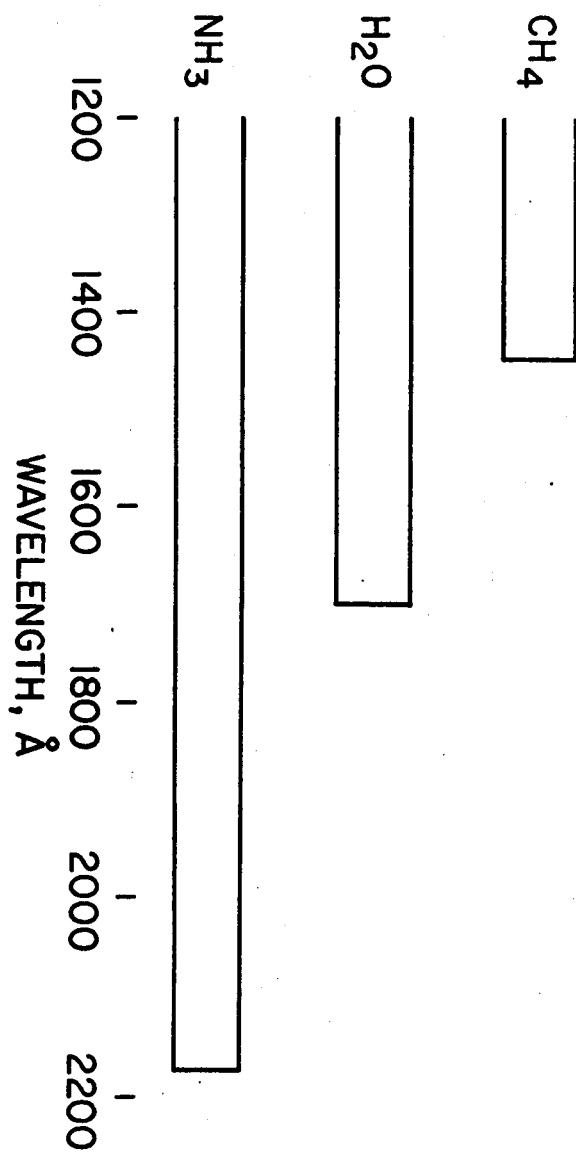


Figure 2

TRANSITION FROM REDUCING TO OXIDIZING ATMOSPHERE

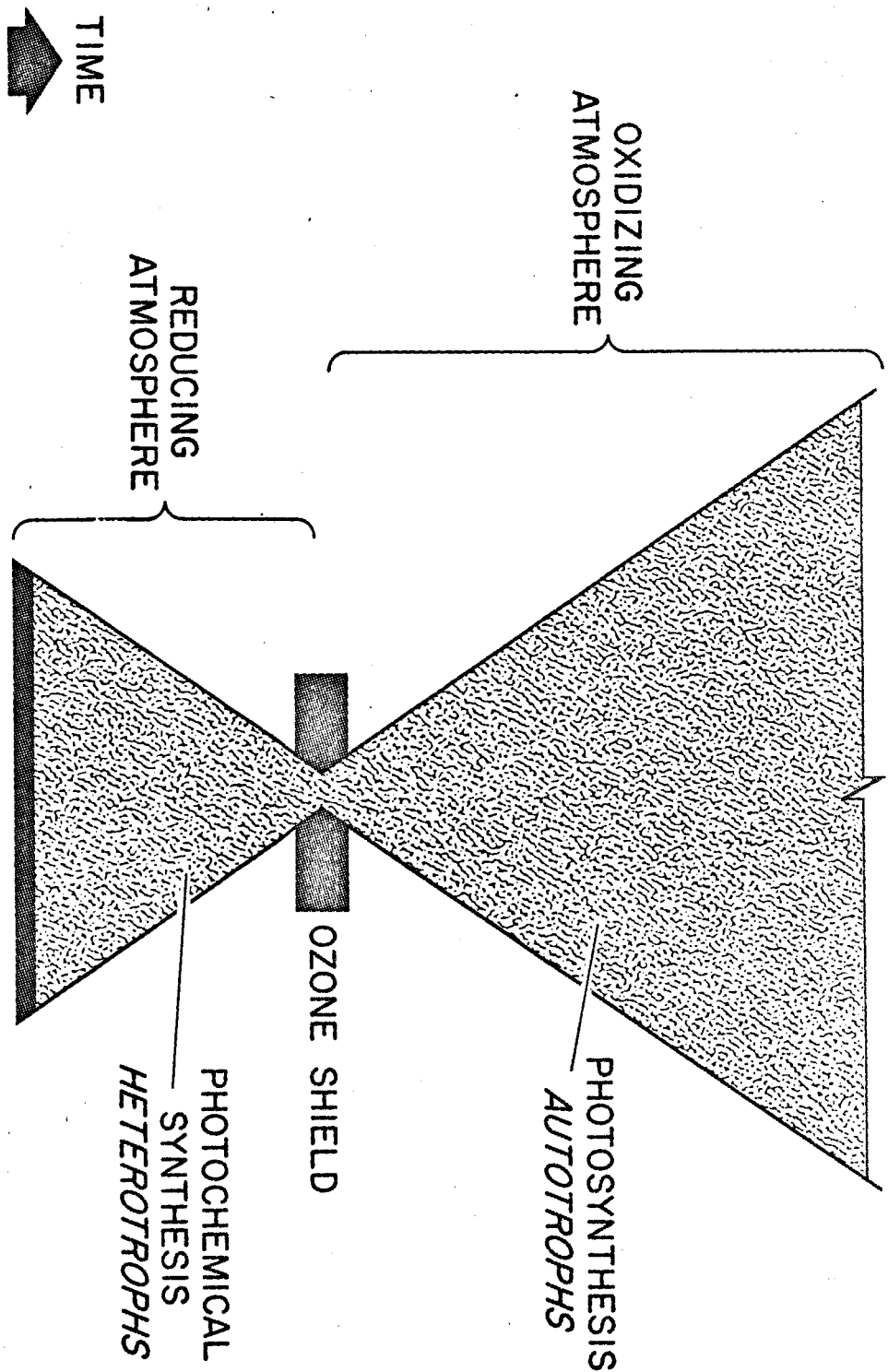
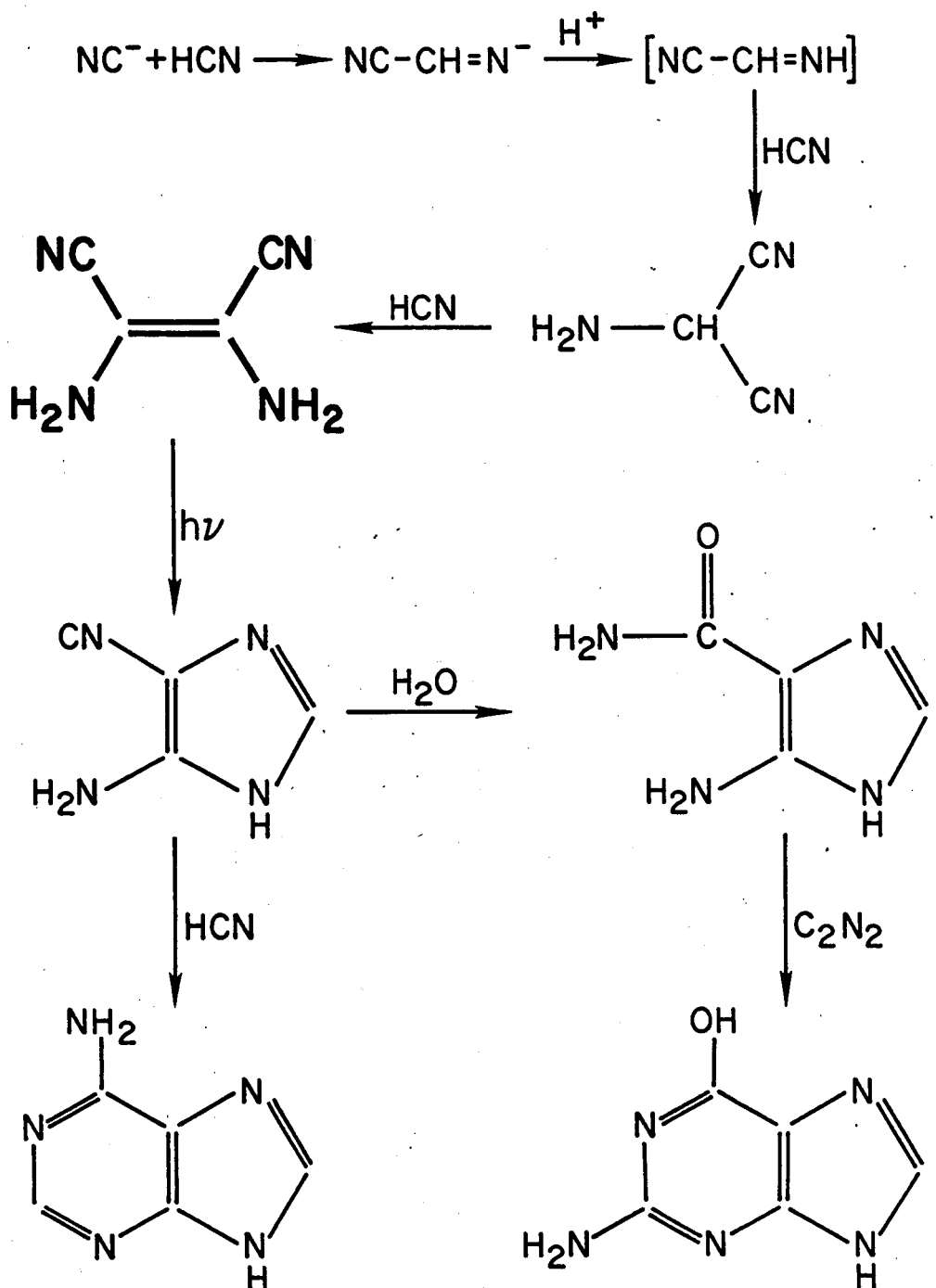


Figure 3

ADENINE AND GUANINE FROM HCN TETRAMER



(ORGEL 1966)

Figure 4

CHEMICAL EQUILIBRIA

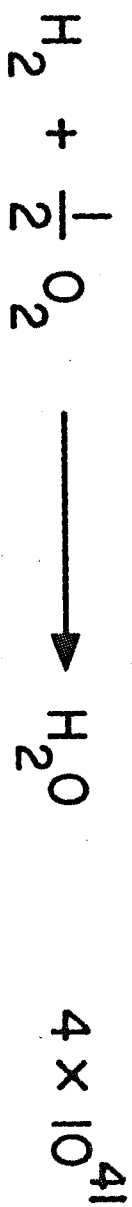
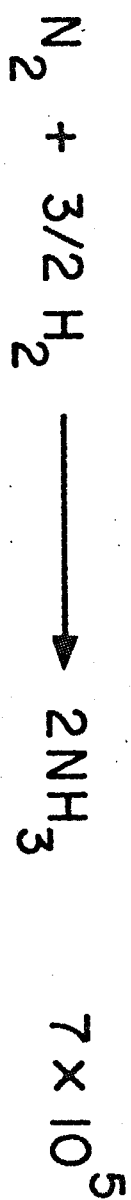
 $K_{25^{\circ}\text{C}}$ 

Table 1

SOLAR ENERGY

WAVELENGTH, Å	ENERGY, cal/cm ² /yr
< 2500	570
< 2000	85
< 1500	16
ALL WAVELENGTHS	260,000

(MILLER AND UREY, 1959)

IONIZING RADIATION

AAA157-7

INVESTIGATOR	RADIATION	MATERIALS	PRODUCTS
GARRISON et al 1951	α	CO ₂ , H ₂ O, Fe ⁺⁺	FORMALDEHYDE FORMIC ACID
DOSE AND RAJEWSKY 1957	X' rays	CO ₂ , CH ₄ , N ₂ NH ₃ , H ₂ O, N ₂	AMINO ACIDS? AMINES
HASSELSTROM et al 1957	β^-	NH ₄ O Ac	GLYCINE ASPARTIC DIAMINO-SUCCINIC
BERGER 1961	p	CH ₄ , NH ₃ , H ₂ O	UREA. ACETAMIDE ACETONE ?
GETOFF et al 1962	γ	CO ₂ , H ₂ O	FORMIC ACID FORMALDEHYDE ACETALDEHYDE
PALM AND CALVIN 1962	β^-	CH ₄ , NH ₃ , H ₂ O, PH ₃ , H ₂	UREA LACTIC ACID GLYCINE ALANINE
ORO 1963	β^-	CH ₄ , C ₂ H ₆ , NH ₃ , H ₂ O, N ₂	AMINO ACIDS HYDROXY ACIDS

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER, MOFFETT FIELD, CALIFORNIA

Table 3

ULTRAVIOLET RADIATION

AA157-6

INVESTIGATOR	RADIATION	MATERIALS	PRODUCTS
BAHADUR 1954	VISIBLE	$\text{HO} \cdot (\text{CH}_2\text{O})_n \cdot \text{H}$ $\text{KNO}_3, \text{FeCl}_3$	SERINE ASPARTIC ACID VALINE LYSINE
GROTH AND WEYSENHOFF 1957	1470 Å - 1296 Å	$\text{CH}_4, \text{C}_2\text{H}_6,$ $\text{NH}_3, \text{H}_2\text{O}$	GLYCINE ALANINE AMINO-BUTYRIC FORMIC ACID PROPIONIC ACID ACETIC ACID
REID 1957	1849 Å	INORGANIC SALTS, CO_2 $\text{HCHO}, \text{NH}_4^+$	GLYCINE ALANINE FORMIC ACID
TERENIN 1957	1000 Å - 2000 Å	$\text{CH}_4, \text{NH}_3,$ H_2O	ALANINE OTHERS?
PAVLOSKAYA AND PASYSKII 1957	> 1800 Å	$\text{HCHO}, \text{NH}_4,$ $\text{NH}_4\text{Cl}, \text{NO}_3$	SERINE GLYCINE GLUTAMIC ACID ALANINE VALINE PHENYLALANINE BASIC AMINO ACIDS?
DODONOVA AND SIDOROVA 1960	1450 Å - 1800 Å	$\text{CH}_4, \text{CO},$ $\text{NH}_3, \text{H}_2\text{O}$	GLYCINE ALANINE VALINE LEUCINE? NORLEUCINE? METHYLAMINE ETHYLAMINE HYDRAZINE UREA FORMALDEHYDE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER, MOFFETT FIELD, CALIFORNIA

Table 4